A PRELIMINARY DETERMINATION OF THE ABSOLUTE ^{14}C/^{12}C RATIO OF OX-I

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ABSTRACT. A preliminary determination of the absolute ^{14}C/^{12}C ratio of the oxalic acid I standard (NBS SRM 4990B) has been made. Using an accelerator mass spectrometry (AMS) system, a known number of radiocarbon ions were implanted in a thin copper foil. The foil was then combusted with the addition of ^{14}C-free carrier material. This resulting gas (which had a known ^{14}C/^{12}C ratio) was graphitized and compared to OX-I material. This comparison yielded an absolute ^{14}C/^{12}C ratio of OX-I. The absolute ^{14}C/^{12}C ratio of OX-I, coupled with knowledge of the specific activity of OX-1, provides an alternative determination of the ^{14}C half-life.

INTRODUCTION

Today, the accepted half-life of radiocarbon is 5700 ± 30 yr (National Nuclear Data Center, Brookhaven National Laboratory, www.nndc.bnl.gov). This value is the weighted average of values obtained from specific activity measurements (Mann et al. 1961; Watt et al. 1961; Olsson et al. 1962; Bella et al. 1968) and is slightly shorter that the value of 5730 ± 40 yr adopted in 1962 by the ^{14}C community as the then-best consensus value (Godwin 1962). Recently, questions have been raised as to the validity of the "accepted" ^{14}C half-life (Broecker 2005; Broecker and Barker 2007; Fairbanks et al. 2005) based on apparent systematic trends and offsets in the ^{14}C calibration curve (cf. Reimer et al. 2004). A significant shift in the ^{14}C half-life would impact our understanding of the ^{14}C calibration curve and would require revision of estimated cosmogenic nuclide production rates over the past 50,000 yr. Although there were no specific reasons to doubt the ^{14}C half-life value, an alternative measurement of the ^{14}C half-life is useful.

The primary standard for ^{14}C dating is oxalic acid I (NBS SRM 4990B). The number of ^{14}C atoms (N_{14}) per gram of carbon in OX-I is given by:

$$N_{14} = A/\lambda \qquad \text{where} \qquad \lambda = \ln 2/T_{1/2} \qquad (1)$$

where A is the specific activity of oxalic acid I and is accepted to be 14.27 ± 0.07 dpm/g normalized to AD 1950 (Stuiver 1980), and $T_{1/2}$ is the absolute ^{14}C half-life. Substituting this into Equation 1:

$$N_{14} = 6.172 \times 10^{10} \text{ atoms/g of OX-I (AD 1950)} \qquad (2)$$

Since the atomic weight of carbon is 12.0107 g, the ^{14}C/C ratio of OX-I is:

$$^{14}\text{C}/^{12}\text{C} = 1.231 \times 10^{-12} \text{ (AD 1950)} \qquad (3)$$

Using an isotopic fractionation of δ^{13}C = –19‰, the ^{14}C/^{12}C ratio of OX-I is then:

$$^{14}\text{C}/^{12}\text{C} = 1.245 \times 10^{-12} \text{ (AD 1950)} \qquad (4)$$

Correcting for decay since 1950, the 2006 ^{14}C/^{12}C ratio of OX-I is:

$$^{14}C/^{12}C = 1.236 \times 10^{-12} \text{ (AD 2006)} \tag{5}$$

If the 2006 absolute $^{14}C/^{12}C$ ratio of OX-I is different from the value in Equation 5, then either the currently accepted ^{14}C half-life is incorrect or the specific activity (AD 1950) of oxalic acid I is not 14.27 dpm/g.

MEASUREMENTS

To measure the absolute $^{14}C/^{12}C$ ratio of oxalic acid I, a known number of ^{14}C ions were implanted in a thin copper foil. The foil was then combusted with the addition of ^{14}C-free carrier material. The resulting gas (which had a known and absolute $^{14}C/^{12}C$ ratio) was graphitized and compared to OX-I. This comparison yielded an absolute $^{14}C/^{12}C$ ratio of OX-I.

The foils used in the measurement were 2.54-cm-square by 25-micron-thick oxygen-free, high-conductivity copper with a metals purity of 99.95%. The foils were obtained from Goodfellow Corporation (Devon, Pennsylvania, USA). Oxygen-free copper was used to minimize the potential for in-situ production and loss of ^{14}CO during implantation. Foils were mounted using the apparatus shown in Figure 1.
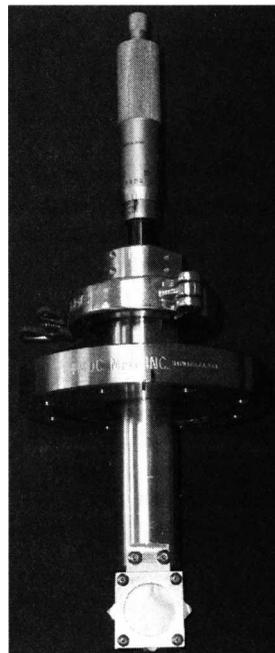

Figure 1 The foil holder showing a mounted copper foil. The holder was mounted directly in front of the AMS detector. Foils could be rotated in and out of the beam using the rotary feedthrough shown at the top. The foil had an "active" area of 2.22 cm diameter defined by the aluminum mounting plate.

Two foils were implanted with ^{14}C at the Keck Carbon Cycle Accelerator Mass Spectrometry (AMS) Laboratory, University of California, Irvine (Irvine, California, USA) and 1 foil was implanted at the National Ocean Sciences AMS Facility, Woods Hole Oceanographic Institution (Woods Hole, Massachusetts, USA). In both laboratories, the foil holder was placed directly after a beam-limiting aperture and directly before the ^{14}C AMS detector. The size of the beam-limiting aperture was smaller than both the "active" area of the foil and the detector opening. A schematic of the setup is shown in Figure 2.
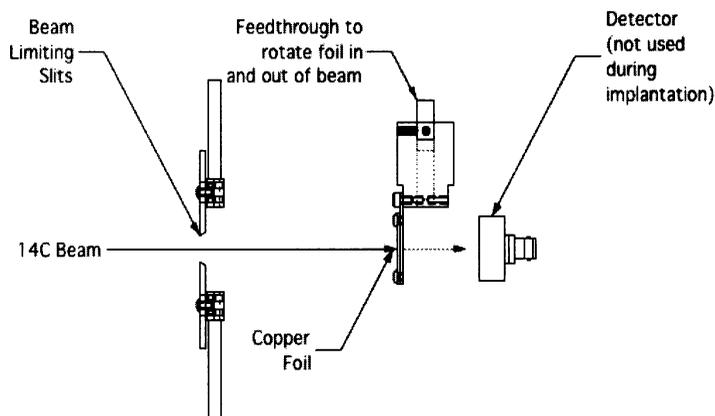
Figure 2 Schematic of the experimental setup

For the implantations, an intense ^{14}C beam was obtained using 12× modern graphite. At Irvine, the ^{14}C ions were accelerated to 1 MeV, while at Woods Hole the ^{14}C ions were accelerated to 10 MeV. Using SRIM (Stopping and Range of Ions in Matter; Ziegler et al. 1985), the range of 1 MeV and 10 MeV ^{14}C ions in copper was calculated to be about 1 and 4 microns, respectively. In both cases, the number of backscattered ions was calculated to be <0.1%.

The implantation cycle was nearly identical at both Irvine and Woods Hole and was as follows:

1. A 12× modern cathode was inserted into the AMS source, and the $^{14}C/^{12}C$ ratio of that cathode was measured in the normal fashion.
2. With the cathode still in the source, the low-energy Faraday cup was inserted.
3. The copper foil was rotated into place in front of the AMS detector.
4. The low-energy Faraday cup was then removed, and the ^{12}C charge on the high-energy off-axis Faraday cup was continuously integrated.
5. When the ^{12}C current started to drop (this was usually after at least an hour), the low-energy Faraday cup was inserted.
6. The copper foil was rotated out of place.
7. The $^{14}C/^{12}C$ ratio of the cathode was again measured in the normal AMS fashion.

The number of implanted ^{14}C ions in a cycle was taken to be the integrated ^{12}C current times the average of the before and after $^{14}C/^{12}C$ ratio of the 12× modern cathode. Corrections were also made for dead time and pileup. The above scheme was repeated with a new cathode until the desired number of ^{14}C ions was implanted in the foil. The number of ions implanted in the 3 foils is shown in Table 1. Due to differences in ion source currents and transmission efficiencies, the implantations at Irvine took about 6 hr each, while at Woods Hole the single implantation required about 18 hr.

After implantation, the copper foils were combusted with the addition of dead (i.e. ^{14}C-free) carrier material. At Irvine, the dead carrier material was coal. At Woods Hole, the dead carrier material was acetanilide. After combustion, the CO_2 was cryogenically purified, and the precise amount of added dead carrier material (and hence the number of added ^{12}C atoms) was determined by measuring the pressure of the CO_2 in a known volume. Table 1 lists the added mass of C (determined volumetrically) and the number of added ^{12}C atoms. At Irvine, the initial combustion (foil + coal + copper oxide) was at 850 °C for 4 hr. The resulting CO_2 was trapped, cleaned, and converted to graphite for AMS analysis. Blank (or non-implanted) foils were also combusted and used as backgrounds in the subsequent AMS analysis. To check for incomplete combustion, the implanted foils and blank foils

Table 1 Measurements.

Foil	Nr of implanted ^{14}C ions[a]	Added C (mg)	Nr of ^{12}C atoms[b]	Absolute ratio ^{14}C/^{12}C	Expected ratio relative to 2006 OX-I[c]	Measured ratio relative to 2006 OX-I[d]	Expected/ measured
UCI-1 (UCIAMS-23529)	6.043 ($\pm$0.042) $\times$ 10^7	0.853 ($\pm$0.004)	4.278 ($\pm$0.019) $\times$ 10^{19}	1.428 ($\pm$0.012) $\times$ 10^{12}	1.1552 ($\pm$0.0127)	1.1622 ($\pm$0.0031)	0.9940 ($\pm$0.0112)
UCI-2 (UCIAMS-23530)	6.531 ($\pm$0.020) $\times$ 10^7	1.150 ($\pm$0.005)	5.766 ($\pm$0.024) $\times$ 10^{19}	1.145 ($\pm$0.006) $\times$ 10^{12}	0.9262 ($\pm$0.0082)	0.9361 ($\pm$0.0020)	0.9895 ($\pm$0.0090)
WHOI-1 (NOSAMS-53201)	2.433 ($\pm$0.036) $\times$ 10^7	0.527 ($\pm$0.003)	2.613 ($\pm$0.013) $\times$ 10^{19}	9.311 ($\pm$0.147) $\times$ 10^{13}	0.7532 ($\pm$0.0119)	0.7738 ($\pm$0.0031)	0.9735 ($\pm$0.0158)

[a]Errors in the total number of implanted ^{14}C ions are based solely on changes in ^{14}C/^{12}C ratios between the start and end of an irradiation. Small corrections were made for dead time and pileup (with each pileup representing 2 implanted ions). Combined, these effects were <3%, and any associated errors were negligible.
[b]Added as coal at UCI and as acetanilide at WHOI. At both UCI and WHOI, the number of ^{12}C atoms was determined volumetrically after combustion.
[c]Ratio of ratios: ^{14}C/^{12}C sample divided by the calculated ^{14}C/^{12}C OX-I ratio assuming an OX-I activity of 14.27 dpm/g C. A half-life of 5700 ± 30 yr (the National Nuclear Data Center, Brookhaven National Laboratory value) was used. A half-life of 5730 yr would decrease this number (and the expected/measured value) by approximately 0.5%.
[d]Ratio of ratios: ^{14}C/^{12}C sample divided by the measured ^{14}C/^{12}C OX-I ratio.

were combusted a second time (foil + coal + copper oxide) and analyzed using AMS. At Irvine, residual ^{14}C was observed, indicating that a few percent of the ^{14}C atoms remained in the foil after the first combustion. In the end, 3 combustion cycles were needed at Irvine to completely extract the implanted ^{14}C from the foil. Learning from the Irvine experience, the foils at Woods Hole were combusted at 850 °C for a much longer time of 12 hr. After combustion, the resulting CO_2 (with a known absolute $^{14}C/^{12}C$ ratio) was graphitized and measured relative to 2006 OX-I at the respective laboratories. Measured values are shown in Table 1.

DISCUSSION

As can be seen from Table 1, preliminary results indicate that the 3 absolute $^{14}C/^{12}C$ ratio measurements of oxalic acid I are all slightly lower than the quoted value. This discrepancy can be explained in 3 ways: 1) in each case we undercalculated the implanted ^{14}C dose in the copper foils; 2) the specific activity of OX-I is lower than 14.27 dpm/g; or 3) the actual ^{14}C half-life is <5700 yr.

We know of no mechanism or process that would have caused us to undercalculate the implanted ^{14}C dose. We should also note that if any implanted ^{14}C remained in the foils after combustion (i.e. we had incomplete combustion), the discrepancy becomes worse.

The specific activity of OX-I was determined using a gas proportional counter (Karlén et al. 1964). For the actual specific activity to be lower than 14.27 dpm/g, the ^{14}C decays in that measurement would have had to have been overcounted. Given the state of gas proportional counting in 1964, we believe it is unlikely decays would have been overcounted using a gas proportional counter.

Therefore, our preliminary data implies a half-life that is shorter than the accepted value by approximately 2 ± 1%. In any event, if the specific activity of OX-I is indeed 14.27 dpm/g, we see no evidence to support the suggestion that the actual ^{14}C half-life is several percent "longer" than 5700 yr (Broecker 2005; Broecker and Barker 2007; Fairbanks et al. 2005).

Our future plans include refinement of our procedures and a remeasurement of the absolute $^{14}C/^{12}C$ ratio of OX-I. We are also exploring alternative (but direct) measurements of the ^{14}C half-life.

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